Current Applied Physics xxx (2010) 1–5

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Gallium nitride light emitter on a patterned sapphire substrate for improved defectivity and light extraction efficiency

Michael A. Mastro [a,*], Byung-Jae Kim [b], Younghun Jung [b], Jennifer K. Hite [a], Charles R. Eddy Jr. [a], Jihyun Kim [b]

[a] US Naval Research Lab., Washington DC 20375, USA
[b] Department of Chemical & Biological Engineering, Korea University, Seoul, 136-713, Republic of Korea

ARTICLE INFO

Article history:
Received 5 October 2010
Accepted 9 November 2010
Available online xxx

Keywords:
A. Semiconductors
B. Epitaxy
D. Recombination and trapping
E. Luminescence

ABSTRACT

Gallium nitride light emitting diodes were deposited on a sapphire substrate that was pre-patterned with an ordered two-dimensional structure. The size and arrangement of the substrate surface pattern was designed to increase the diffraction and extraction of light from the device as well as define the grain size and thus dislocation density of the GaN crystal. A close-packing of self-assembled SiO_2 nanospheres was used as the sacrificial etch mask. The etch process transferred a two-dimensional pattern into the sapphire substrate with a peak-to-peak dimension of approximately 250 nm. The distance was selected to match the emission wavelength in the crystal for optimal light scattering. Additionally, the dimensions of the crystal artificially defined the grain size of the GaN in contrast to the kinetically controlled grain size in a standard GaN on sapphire growth process.

Published by Elsevier B.V.

1. Introduction

Gallium nitride is the basis of the several billion-dollar UV, blue, and green light emitting diode industry. Despite years of progress the standard approach to deposit the LED structure on sapphire is still plagued by a high density of dislocations as well as low external extraction efficiency. The difference in the refractive index between the semiconductor and the package/air limits extraction of photons generated in the active region that propagate outside of the light extraction cone [1–4].

Surface photonic crystal structures are effective at redirecting wavelength-specific light out of the crystal. Unfortunately, the dimensions of a photonic crystal designed for a GaN-based emitter are on the order of 250 nm [5], which is difficult to implement in a high-volume lithography process – although self-assembled approaches have proven promising [6]. A much simpler manufacturing approach is to roughen the GaN surface or the sapphire substrate (in a flip-chip configuration) to create an ensemble of sub-micron scattering sites [7]. A recent variant of this approach is to roughen the surface of the sapphire substrate prior to growth [8]. The subsequently grown LED will possess, at the semiconductor/sapphire interface, a high density of scattering sites that redirect light that would otherwise suffer from total internal reflection.

This paper presents an approach to form a photonic crystal like structure on the sapphire substrate for more efficient scattering of photons. A second advantage of this approach is that the two-dimensional structure in the sapphire can be designed to manipulate the coalescence of GaN grains at the initial stages of growth.

Epitaxy of GaN on sapphire is dissimilar to the near lattice-matched epitaxy of GaN on SiC as well as the homoepitaxy of traditional III-V semiconductors on their native III-V substrate. The large difference in lattice spacing between the GaN and sapphire as well as the non-polar nature of the sapphire crystal is accommodated by a low-temperature AlN (or GaN) nucleation layer. The subsequently grown GaN layer initially forms as large grains that reach heights of tens to hundreds of nanometers prior to coalescence of the grains. Internally the grains are generally free of dislocations. Edge and screw dislocations accumulate at the grain boundaries and serve to accommodate intra-grain twist and tilt, respectively. The importance of the coalescence mechanism in determining the density of dislocations is well known. Simple optimization of process parameters is used to enhance the size of the grain and thus lower the dislocation density. An extension of this process optimization is the delayed coalescence technique, which intentionally impedes lateral growth of small grains to form larger (single-crystal) grains. All growth optimization approaches rely on the intrinsic kinetics of the growth process to determine the grain size distribution.

Herein, we show a two-dimensional periodicity in the sapphire substrate controls the grain formation mechanism. Specifically,

* Corresponding author.
E-mail address: michael.mastro@nrl.navy.mil (M.A. Mastro).

1567-1739/$ – see front matter Published by Elsevier B.V.
doi:10.1016/j.cap.2010.11.032

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **OCT 2010**	2. REPORT TYPE	3. DATES COVERED **00-00-2010 to 00-00-2010**

4. TITLE AND SUBTITLE **Gallium nitride light emitter on a patterned sapphire substrate for improved defectivity and light extraction efficiency**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,4555 Overlook Ave SW,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Gallium nitride light emitting diodes were deposited on a sapphire substrate that was pre-patterned with an ordered two-dimensional structure. The size and arrangement of the substrate surface pattern was designed to increase the diffraction and extraction of light from the device as well as define the grain size and thus dislocation density of the GaN crystal. A close-packing of self-assembled SiO2 nanospheres was used as the sacrificial etch mask. The etch process transferred a two-dimensional pattern into the sapphire substrate with a peak-to-peak dimension of approximately 250 nm. The distance was selected to match the emission wavelength in the crystal for optimal light scattering. Additionally, the dimensions of the crystal artificially defined the grain size of the GaN in contrast to the kinetically controlled grain size in a standard GaN on sapphire growth process.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**5**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

a self-assembled etch mask defines the peaks in the etched sapphire surface, which directly determines the GaN grain size and geometry.

2. Experimental

Self-assembled silica (SiO_2) nanospheres with an average diameter of 250 nm were prepared by the Stöber process, which involves the hydrolysis of tetraethylorthosilicate in ethanol in the presence of deionized water and ammonia [9]. The size of SiO_2 nanospheres was controlled by adjusting the mole fraction of ammonia. A colloidal solution of nanospheres in ethanol was dispersed onto a sapphire substrate to form a two-dimensional configuration. Closer examination of the diameter of the SiO_2 nanospheres in Fig. 1 reveals a secondary distribution of particles with a diameter of approximately 200 nm. The two-dimensional packing of SiO_2 nanospheres acted as a self-assembled mask to define an approximation to negative image in the substrate. The patterned sapphire substrate (PSS) was prepared by dry etching in a multiplex ICP (STS) system at a pressure of 5 m Torr. A mixture of Cl_2 (7.5 sccm) and BCl_3 (30 sccm) at an RF power of 150 W and coil power of 600 W yields an etch rate of sapphire of 100 nm/min [10].

Gallium nitride single quantum well LEDs were grown by metal-organic chemical vapor deposition (MOCVD) directly on etched and unetched sapphire substrates. Growth was carried out in a modified vertical impinging flow CVD reactor. Following a 20 min NH_3 nitridation procedure at 680 °C, a 25 nm AlN buffer layer was deposited at 680 °C and 50 Torr. Subsequently, a 1.5 μm n-type GaN:Si/25 nm $Al_{0.1}Ga_{0.9}N$/10 nm GaN/25 nm $Al_{0.1}Ga_{0.9}N$/300 nm GaN:Mg structure was deposited at 1020 °C and 250 Torr. The n- and p-type doping of GaN was accomplished with disilane and Cp_2Mg, respectively. As an n-type electrode, a Ti/Al/Ni/Au (20 nm/40 nm/30 nm/80 nm) layer was deposited by electron-beam evaporator, followed by annealing at 750 °C for 30 s to achieve the ohmic contact. Then, a Ti/Au (40 nm/100 nm) with a very thin Ni/Au(2 nm/2 nm) layer was deposited to form the p-type electrode. Current-voltage behavior was obtained by Agilent 4155C parameter analyzer. Electroluminescence spectra were measured by Ocean Optics USB 2000 + spectrometer connected to the probe station.

3. Results and discussion

A colloidal solution of SiO_2 nanospheres in ethanol was dispersed on the sapphire substrate and allowed to dry. Colloidal dispersions of hard spheres are well known to form a two-dimensional face centered cubic crystal at a volume fraction 0.536 with the closest packed plane of FCC crystal, the (111) plane, being parallel to the substrate plane [11]. Point defects such as vacancies can be seen in the SEM micrograph in Fig. 1. This is expected as it is entropically favorable for the system to have some vacancies [16].

Subsequent dry-etching via an inductively coupled plasma using a gas mixture of BCl_3 and Cl_2, transferred the pattern into the sapphire substrate with the lowest etch depth at the former center of the SiO_2 nanosphere. The periodic undulations in the sapphire substrate are observable in the cross-sectional SEM image in Fig. 2. Further visible in Fig. 2 is that the patterned structure in the sapphire substrate defines the grain size of the GaN crystal. The grain boundaries, which appear as dark lines, are presumably defined by vertical threading dislocations.

The dominant defect in GaN films grown along the [0001] direction are threading dislocations with a [0001] line direction. The three main types are edge ($\mathbf{b} = 1/3 < 11{-}20>$), mixed ($\mathbf{b} = 1/3 < 11{-}23>$), and screw ($\mathbf{b}{=}<0001>$). The concentration of pure screw dislocations is typically less than 2%; however, a larger percentage of the screw-component is present as mixed (edge + screw) dislocations. The lattice distortion of an edge dislocation accommodates lattice twist, a screw dislocation accommodates lattice tilt, and a mixed dislocation accommodates tilt and twist. Symmetric ω {000l} reflections are sensitive to distortion of the crystal lattice spacing normal to the (0001) surface; therefore screw dislocations and the screw component from mixed dislocations broaden the ω {000l} rocking curves. Edge dislocations have a Burgers vector that lies within this plane and do not affect the symmetric ω {000l} reflections.

The opposite mechanism arises for planes perpendicular to the surface, which are distorted by edge dislocations but are not affected by screw dislocations. The finite thickness of thin films makes it practically impossible to diffract from a sufficient volume of crystal to measure the distortion of the lattice perpendicular to the surface. A single high angle reflection can approximately measure the edge-component in the crystal; however, any reflection at an interplanar angle will be broadened by both edge and screw dislocations.

The mosaic crystal model assumes the film consists of perfect crystal grains with inter-grain tilt and twist present at the boundaries. The mosaic model describes well the growth of GaN on sapphire, which is known to proceed by coalescence of low-defect grains with a high density ($>1 \times 10^8$ cm^{-2}) of threading dislocations demarcating the grain boundaries.

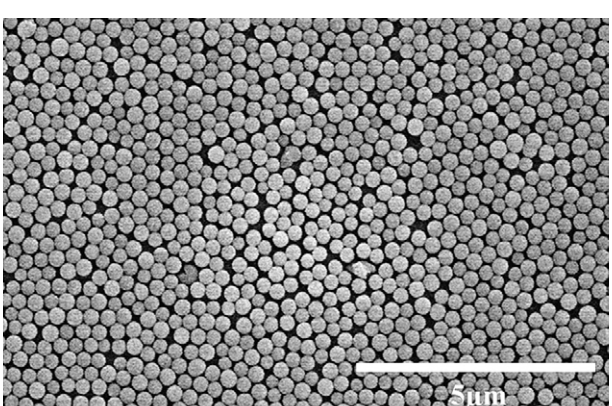

Fig. 1. Top-view SEM image of a self-assembled two-dimensional array of SiO_2 nanospheres on the surface of the GaN LED before ICP etch.

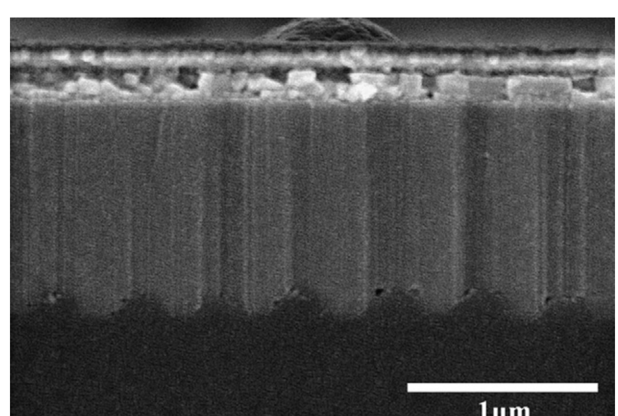

Fig. 2. Cross-sectional SEM of a GaN LED grown on sapphire substrate with a two-dimension etch pattern. The peaks in the sapphire define the grain boundaries in the GaN film. The texture at the top of the LED is an artifact of the cleaving process.

Please cite this article in press as: M.A. Mastro, et al., Gallium nitride light emitter on a patterned sapphire substrate for improved defectivity and light extraction efficiency, Current Applied Physics (2010), doi:10.1016/j.cap.2010.11.032

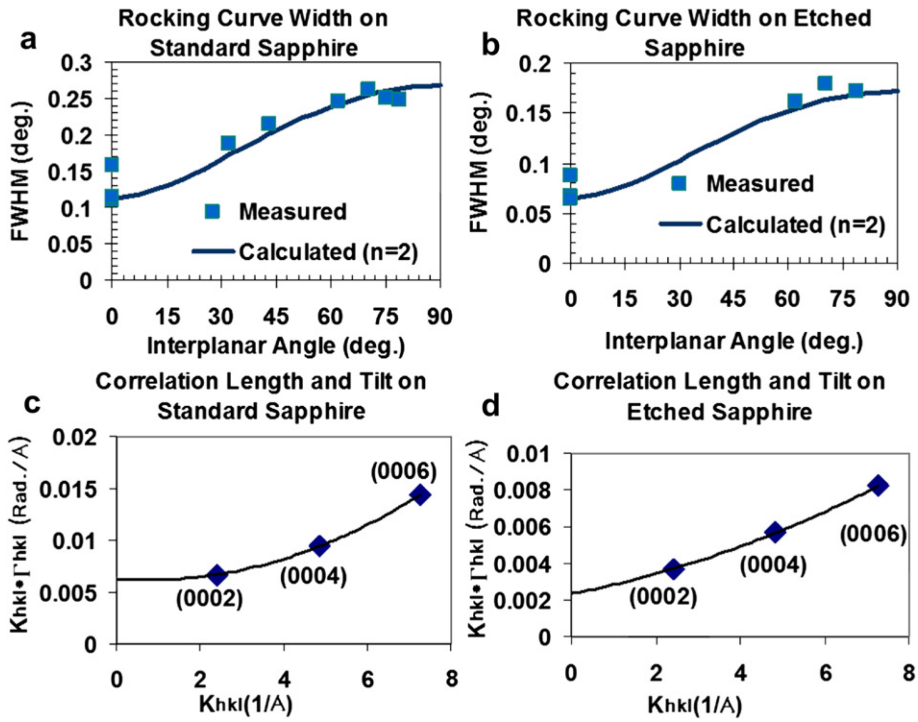

Fig. 3. X-ray rocking curve width analysis of a GaN LED on (a,c) a standard substrate and (b,d) an etched substrate. (a,b) FWHM of rocking curves for reflecting lattice planes as a function of inclination angle relative to the surface normal. The fitted curve of the mosaic crystal model yields (a) $DD_{screw} = 3.36 \times 10^8$ and $DD_{edge} = 4.91 \times 10^9$ on standard sapphire and (b) $DD_{screw} = 1.11 \times 10^8\ cm^{-2}$ and $DD_{edge} = 2.03 \times 10^9\ cm^{-2}$ on etched sapphire. Graphical separation plot for symmetric ω scans yields a (c) $L_{||} = 153.1$ nm and tilt angle $\Gamma_y = 0.107°$ on standard sapphire and (d) $L_{||} = 254.2$ nm and tilt angle $\Gamma_y = 0.0614°$ on etched sapphire.

The components of the mosaic (surface normal) tilt and (in-plane) twist can be extracted from a series of symmetric and skew-symmetric reflections. A set of interplanar rocking curve widths is a convolution of the tilt, twist and coherence length of the crystal as described by

$$\Gamma_{hkl}^{n} = (\Gamma_y \cos\chi)^n + (\Gamma_z \sin\chi)^n + (2\pi/L)^n / K_{hkl}^{n}$$

where Γ_{hkl} is the FWHM of the Bragg peak, $K_{hkl} = (4\pi/\lambda)(\sin\chi)$ is the reciprocal lattice vector, χ is the interplanar angle, and Γ_{hkl} is rotational distribution about K_i (i = x,y,z) [12].

The global behavior of the fitted peakwidths indicate that a Gaussian fit ($n = 2$) is optimal. Fig. 3a,b displays the rocking curve width for a series of reflections as a function of crystal plane direction relative to the surface normal. For example, the symmetric (0002), (0004), and (0006) reflections are at an interplanar angle of zero as these planes are parallel to the c-plane surface. A least-squares fit of the tilt, twist and coherence length of the crystal is graphically displayed as a solid line in Fig. 3a,b. The patterning of the sapphire substrate led to a 2.40x reduction in edge dislocations and 3.02x reduction in screw dislocation (component) compared to the dislocation density in the GaN structure grown on a standard sapphire substrate.

Fig. 3c and d contain graphical representations of a modification of the Williamson-Hall model for an interplanar angle of zero. The y-axis intercept $(2\pi/L_{||})^2$ of this plot yields the symmetric coherence length, $L_{||}$. The x-ray analysis of the GaN film on the etched substrate indicated that the coherence length ($L_{||} = 254.2$ nm) was approximately equal to the dimensions of the patterned sapphire substrate. In contrast, the analysis of the GaN crystal on the standard sapphire substrate extracted a shorter coherence length ($L_{||} = 153.1$ nm). As the films were grown under identical situations, this x-ray result indicates that formation mechanism and resultant average grain size of a GaN thin film is highly dependent on sub-micron surface pattern on the sapphire substrate.

Lee et al. showed that the extraction of dislocation density in a GaN crystal by an x-ray analysis similar to that given above agrees well with TEM analysis of an identical sample. The advantage of x-ray analysis is that the sampled area in x-ray (of approximately 10 mm^2) is much larger the typical area examined in TEM.

For similar reasons, we examined the sample near surface using a non-destructive determination of dislocation type and Burgers vector direction using electron channeling contrast imaging (ECCI) inside a scanning electron microscope [13]. Forescattered electron intensity fluctuations generated by threading dislocations exhibit characteristic spatial profiles indicative of dislocation type (screw, edge) and Burgers vector direction as well as grain boundaries [14]. An ECCI image of the (0001) GaN film surface is presented in Fig. 4. Detailed examination of dark-to-light intensity fluctuations allows determination of the location and type of threading dislocations penetrating to the surface. To guide the eye, larger blue and smaller white circles imposed onto the image show the location of dislocations that outline the grain boundaries. The distribution of the grain boundary presents a bi-modal distribution peaked at approximately 200 and 250 nm. Examination of the SEM picture in Fig. 1 of the self-assembled SiO_2 nanospheres shows that a small yet significant fraction of the nanospheres have a diameter of approximately 200 nm.

A functional GaN LED was fabricated on the standard sapphire as well as the patterned sapphire substrate. The electroluminescence and current/voltage characteristics are displayed in Fig. 5. An inclined SEM image of the metallization on the LED surface is presented in the Fig. 5a inset. The main electroluminescence emission peak occurs at 365 nm (Fig. 5a). The optical image of ultraviolet emission of LED is pictured the Fig. 5b inset. The internal efficiency of an LED is highly dependent on the dislocation

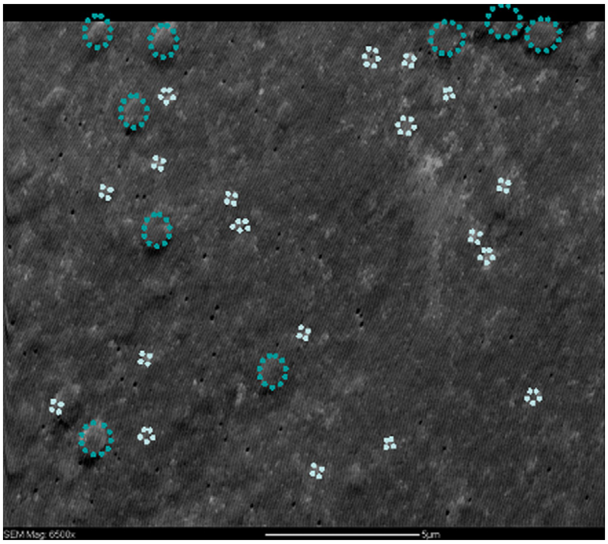

Fig. 4. Experimental ECCI image of a GaN film surface. Intensity fluctuations are apparent across the surface due to electron channeling and local strain induced by TDs. A subset of the dislocations penetrating to the surface and imaged by ECCI are highlighted with blue or white dots to emphasize threading dislocations decorating the boundary of a GaN grain. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

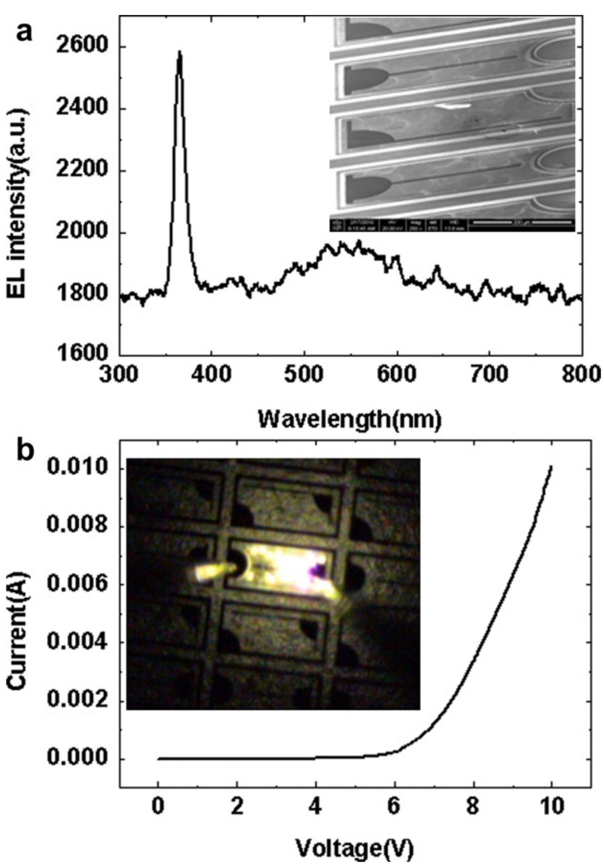

Fig. 5. Electroluminescence (a) spectrum and (b) current/voltage measurement of a LED on a PSS. The n- and p-metallization is observable in the inset in (a) of an angled plan-view SEM image of the LED surface. (b inset) A real-color image of the LED operating at 10 mA.

density and the extraction efficiency is highly dependent on geometry of the sample including the sapphire surface patterning employed in this study. Work is underway to deconvolute these two effects.

This focus of the work is to both control the nature of the GaN coalescence process to create larger GaN grains with a resultant lower density of dislocations at the grain boundaries; and to enhance the extraction of photons internally generated at the active region by creating a two-dimensional photonic pattern with dimensions that approximate the optical wavelength. Su et al. [15] used a similar approach based on either self-assembled SiO_2 nanosphere etch mask (diameter = 450 nm) or conventional lithography (diameter = 2 μm, 3 μm); however, the resultant dimensions in the sapphire are more akin to random light scattering than a photonic effect. Su et al. did observe a small dependence on x-ray rocking curve width and etch pit density but the mechanism was not explained.

It is conceivable that the ability to control of the grain size with a patterned substrate has an upper limit that depends on the kinetically determined grain size on a standard sapphire substrate. For example, an average grain size of 153 nm was extracted from x-ray diffraction data of a GaN thin film on sapphire. The size of this grain is determined by the kinetics of the particular growth process parameters and it is known that the grain size can be slightly increased based on process optimization. It is unlikely that the grain size could be increased to an infinitely large extent by solely increasing the dimensions of the surface pattern. At some size, e.g., 3 μm, the surface pattern will be effectively imperceptible to the kinetics of the grain formation mechanism. It follows that the 250 nm spacing described in this paper is below this upper limit for our particular growth parameters.

4. Summary

A patterned sapphire substrate was employed to define the grain size of a GaN thin film and the dimension of the pattern was selected match the optical wavelength of the emitted light for photonic-like enhancement of light extraction out of the LED structure. The x-ray and ECCI analysis established that the patterned substrate altered the growth habit of the GaN crystal to match the underlying two-dimensional structure. The increased grain size was effective for decreasing the density of edge and screw dislocations in the LED structure.

Acknowledgements

This research was supported by the Carbon Dioxide Reduction and SequestrationCenter, one of the 21st Century Frontier R&D Program funded by the Ministry of Education, Science and Technology of Korea. The research at US Naval Research Lab was supported by the office of the Naval Research.

References

[1] M.A. Mastro, J.D. Caldwell, R.T. Holm, R.L. Henry, C.R. Eddy Jr., Adv. Mater. 20-1 (2008) 115.
[2] T. Fujii, Y. Gao, R. Sharma, E.L. Hu, S.P. DenBaars, S. Nakamura, Appl. Phys. Lett. 84 (6) (2004) 855.
[3] D.H. Kim, C.O. Cho, Y.G. Roh, H. Jeon, Y.S. Park, J. Cho, J.S. Im, C. Sone, Y. Park, W.J. Choi, Q.H. Park, Appl. Phys. Lett. 87 (2005) 203508.
[4] T.A. Truong, L.M. Campos, E. Matioli, I. Meinel, C.J. Hawker, C. Weisbuch, P.M. Petroff, Appl. Phys. Lett. 94 (2009) 023101.
[5] M.A. Mastro, C.S. Kim, M. Kim, J. Caldwell, R.T. Holm, I. Vurgaftman, J. Kim, C.R. Eddy Jr., J.R. Meyer, Jap. J. Appl. Phys. 47 (2008) 7827.
[6] B.J. Kim, H. Jung, J. Shin, M.A. Mastro, C.R. Eddy Jr., J.K. Hite, S.H. Kim, J. Bang, J. Kim, Thin Solid Films 517 (2009) 2742.
[7] B.-J. Kim, H. Jung, H.-Y. Kim, S.H. Kim, J. Bang, J. Kim, M.A. Mastro, R.T. Holm, J.K. Hite, C.R. Eddy Jr., Thin Solid Films 516 (21) (2008) 7744.

[8] Z.H. Feng, Y.D. Lu, K.M. Lau, J. Cryst. Growth 272 (2004) 327.
[9] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[10] Y.P. Hsu, S.J. Chang, Y.K. Su, J.K. Sheu, C.H. Kuo, C.S. Chang, S.C. Shei, Opt. Mater. 27 (2005) 1171–1174.
[11] K.W. Tan, G. Li, Y.K. Koh, Q. Yan, C.C. Wong, Langmuir 24 (17) (2008) 9273 P. N. Pusey, W. van Megan, Nature, vol. 320, pp. 320–323, 1986.
[12] S.R. Lee, A.M. West, A.A. Allerman, K.E. Waldrip, D.M. Follstaedt, P.P. Provencio, D.D. Koleske, C.R. Abernathy, Appl. Phys. Lett. 86 (2005) 241904.
[13] Y.N. Picard, M.E. Twigg, J.D. Caldwell, C.R. Eddy Jr., M.A. Mastro, R.T. Holm, Scripta Materialia 61 (2009) 773.
[14] Y.N. Picard, J.D. Caldwell, M.E. Twigg, C.R. Eddy Jr., M.A. Mastro, R.L. Henry, R.T. Holm, P.G. Neudeck, A.J. Trunek, J.A. Powel, Appl. Phys. Lett. 91 (2007) 094106.
[15] Y.K. Su, J.J. Chen, C.L. Lin, S.M. Chen, W.L. Li, C.C. Kao, J. Cryst. Growth 311 (2009) 2973.
[16] K.W. Tan, Y. Koon Koh, Y.-M. Chiang, C.C. Wong, Langmuir 26 (10) (2010) 7093.

Please cite this article in press as: M.A. Mastro, et al., Gallium nitride light emitter on a patterned sapphire substrate for improved defectivity and light extraction efficiency, Current Applied Physics (2010), doi:10.1016/j.cap.2010.11.032